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Chemical Analyses - Digestion of sediment, sludge, soil, biowaste and waste for the extraction of nitric acid soluble fraction of trace elements

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Introduction

This document is developed in the project 'Horizontal'. It is the result of a desk study on digestion of solid matrices by using nitric acid and aims at a modular digestion standard for the subsequent analyses of elements. After discussion with all parties concerned in CEN, the digestion method described in this study will be developed further as a modular horizontal method and validated in the project 'Horizontal'.

Until now, test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods, steps such as sampling, extraction, release or other processing, analyses, etc. were often included. In this approach, it was necessary to develop, edit and validate similar procedural steps over and over again for each other product. Consequently, this resulted in a lot of duplicate work. To avoid such duplication of work, parts of a testing procedure often referred to parts of test methods from other TCs. However, the following problems are often encountered while using references in this way: 1) often the referenced parts are not edited in a way so that they can easily be referred to, 2) often the referenced parts are not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements of the test procedure could be described in a way that they can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis a horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in a test procedure, in this case the digestion step, and not the whole test procedure (from sampling to analyses).

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics, it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

This standard is a module, for analyses of trace elements in solid matrices. This module concerns the digestion with nitric acid for the subsequent analysis of elements.

The other horizontal modules that will be available in due time are to be found in the informative annex [xxx], which contains a brief overview of the modules that are or will be worked out in the project 'Horizontal'.

The draft horizontal standard was prepared on the basis of existing Nordic standards for the digestion of solid matrices. Furthermore it was prepared with a view to the modular principle in the existing EN and ISO standards for the digestion of water samples - using either aqua regia or nitric acid - which are applicable to all types of waters. The draft standard is developed in parallel to the draft horizontal standard for digestion of solid matrices using aqua regia.

The texts of Chapters 1 to 9 are normative; annexes are normative or informative, as stated in the top lines of the annexes. Notes in the text are informative.

1 Scope

This Part of EN XXXXX specifies a method for the digestion of sediment, sludge, soil, biowaste and waste.

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The nitric acid digestion method is empirical and it might not necessarily release elements completely. However, for most environmental applications the result is fit for the purpose.

Information of comparability to aqua regia method - *To be adjusted in accordance with the comparative study and validation study*

Solutions produced by the method are suitable for analysis e.g. by atomic absorption spectrometry (FAAS, HGAAS, CVAAS, and GFAAS), inductively coupled plasma emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

NOTE The degree to which analytes are brought into solution suitable for subsequent analysis may depend on the principle of the subsequent analysis. Some analytical methods require the element in solution independent of its chemical state, others require a specific valence or a specific ionic species, for instance hydride atomic spectrometry, photometry and electrochemical methods.

2 Normative references

This European Standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN XXXX:200X	Digestion method - extraction of aqua regia soluble elements from soil, sludge and biowaste
EN ISO 3696:1995	Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)
EN XXXX:200X	Determination of dry matter and water content on a mass basis - gravimetric method
EN XXXX:200X	Pre-treatment ... standard to be processed ...(Horizontal)

3 Terms and definitions

For the purposes of this standard, the following terms and definitions apply:

3.1 digestion

mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacted with a reagent.

3.2 aqua regia

digestion solution obtained by mixing 1 volume of nitric acid (65 - 70% m/m) and 3 volumes of hydrochloric acid (35 - 37% m/m).

3.3 sample

portion of material selected from a larger quantity of material.

3.4 laboratory sample

sample or subsample(s) sent to or received by the laboratory.

3.5 test sample, analytical sample

sample, prepared from the laboratory sample from which test portions are removed for testing or analysis.

3.6 test portion, analytical portion

quantity of material of proper size for measurement of the concentration or other properties of interest, removed from the test sample.

NOTE 1: The test portion may be taken from the laboratory sample directly if no preparation of sample is required (e. g. with liquids), but usually it is taken from the prepared test sample.

NOTE 2: A unit or increment of proper homogeneity, size and fineness, needing no further preparation, may be a test portion.

3.7 dry matter

the remaining mass fraction of a sample after the specified drying process. It is expressed in percentage or as grams per kilogram.

3.8 digestion vessel

special flask where test portion and acid are filled in and the digestion is performed.

4 Safety remarks

All this work has to be performed by skilled persons. The reagents used within this EN are strongly corrosive and partly very toxic. Safety precautions are absolutely necessary due to strong corrosive reagents, high temperature and high pressure.

All procedures have to be performed in a hood or in closed force-ventilated equipment. By the use of strong oxidising reagents the formation of explosive organic intermediates is possible, especially when dealing with samples with a high organic content. Do not open pressurised vessels before they have cooled down. Avoid contact with the chemicals and the gaseous reaction products. Samples and solutions have to be disposed of according to regulations.

5 Principle

The test portion is digested with nitric acid (7 mol/L) in an autoclave at 200 kPa for 120°C or 30 minutes. After digestion the digest is filtered, if necessary, and diluted to a fixed volume with water.

6 Reagents

During analysis, use only reagents of recognised analytical grade that meet the purity requirements of the subsequent analysis. Verify their purity by performing a blank test.

6.1 Water

Comply with grade 2 of EN ISO 3696 or better. The water for preparation of reagent shall meet the requirement of the subsequent analysis.

6.2 Nitric acid

$c(\text{HNO}_3) = 15,8 \text{ mol/L}$, $\rho = 1,4 \text{ kg/L}$

Sub-boiling distilled. Other grade may be used provided it is ascertained that the reagent is of sufficient purity to permit its use without decreasing the accuracy of the subsequent analysis.

Nitric acid is available both as $\rho(\text{HNO}_3) = 1,40 \text{ kg/L}$, approximately 65% by mass, and $\rho(\text{HNO}_3) = 1,42 \text{ kg/L}$, approximately 69% by mass. Both are suitable.

6.3 Nitric acid, 7 mol/L

Dilute under careful stirring one volume of nitric acid (6.2) with one volume of water (6.1).

7 Apparatus

All glassware and plasticware shall be adequately cleaned and stored in order to avoid any contamination.

7.1 Digestion vessel

Temperature- and pressure-resistant and having a nominal volume of 100 ml.

The inner wall of the vessel shall be inert and shall not release substances to the digest in excess of the purity requirements of the subsequent analysis. The vessel shall be suitable for the safe application in the temperature and pressure range applied.

NOTE Digestion vessels may be cleaned in e.g. 10% nitric acid.

7.2 Autoclave

Pressure adjustable enabling it to obtain and maintain a temperature of 120°C for at least 30 minutes.

The accuracy of the temperature and pressure measurement or control shall guarantee working at the specified temperature interval. This includes traceability to national or international temperature and pressure standards.

7.3 Filter paper

cellulose-based ashless type, hardened and resistant to nitric acid.

7.4 Volumetric flask

usually of a nominal capacity of 50 mL or 100 mL.

7.5 Graduated pipettes or dispensers

7.6 Analytical balance

with an accuracy of 0,1 mg or better.

8 Interferences and sources of error

8.1 General informations

Due to the volatility of some compounds, it is of great importance to take care that the sample is not heated before the digestion and that any volatile reaction products formed during the digestion are not allowed to escape.

Grinding or milling samples includes a risk of contamination of the sample by the environment (air, dust, wear of milling equipment). Due to elevated temperature, loss of volatile compounds is possible. For the determination of elements forming volatile compounds (e.g. Hg, As, Pb), special care has to be taken at sample pre-treatment.

The use of the described digestion procedures may leave large parts of the sample undissolved. This includes the risk of low accuracy.

High acid and solute concentrations in the digest cause interferences, which need to be properly addressed during determination.

Care shall be taken to ensure that all of the test portion is brought into contact with the acid mixture in the reaction vessel.

Some elements of interest can be lost because of precipitation with some ions of the solution. This is the case for insoluble chlorides, fluorides and sulphates, for example. In this case, the precipitate can be analysed separately.

In the case of filtration of the digested solution, it is necessary to take care that the filtration procedure does not introduce contamination.

9 Pre-treatment

9.1 Pre-treatment of test portion

The test portion should be transferred into the vessel after a pre-treatment of the laboratory sample to result in homogeneous and representative test portions out of the laboratory sample. This procedure shall not change the concentration of the elements of interest.

NOTE: For soil samples it is common to use the fraction < 2mm.

The mass of laboratory samples shall be sufficient for the multiple digestion procedures and the determination of the dry matter.

To be further adjusted according to result of validation study and to possible horizontal standard on pre-treatment.

9.2 Mass of test portion

The mass of test portion for a single digestion has to be selected in a way so that it is representative of the laboratory sample.

For representativity reason, a mass above 200 mg is to be preferred.

10 Procedure

10.1 Blank test

The reagent blank test shall be carried out in parallel with the determination, by the same procedure, by the use of the same quantities of all the reagents as in the determination but omitting the test portion.

NOTE: The measurement of a blank is introduced to determine the contribution of the extracting solution, glassware and filter paper used.

10.2 Digestion in an autoclave

10.2.1 Amount of samples

Weigh into the digestion vessel an amount equal to 5 g dried sample, for samples rich in organic carbon a maximum of 2 g of the sample, accurately at 0,1 mg, prepared according to clause 8 and transfer it into the vessel (7.1).

10.2.2 Digestion

Add 20 mL \pm 1 mL of HNO_3 (6.3) to the digestion vessel with test portion.

Swirl and allow the mixture to stand until any visible reaction has stopped.

Cap the digestion vessel and place it in the autoclave (7.2).

Adjust the pressure relief to the value equivalent to the vapour pressure of water at the required digestion temperature. Run the autoclave. When it has reached 120°C, maintain the temperature for 30 minutes.

Allow the digestion mixture to cool down to room temperature.

Uncap and vent the digestion vessels in a fume hood.

Decant the sample into the acid-cleaned volumetric flask (7.4). In order to transfer the analytes quantitatively, wash the digestion vessel water (6.1) and decant the washings. Collect the water in the same volumetric flasks. Fill the volumetric flasks to the mark after addition of any reagent that is required for subsequent sample handling and analyses.

The extract is ready for determination.

NOTE: If the digested mixture contains particles that might clog the nebulizers of the measurement apparatus or that might interfere with the injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or be filtered. In the case of filtration, dilute the content of the vessel before filtering, rinse and then dilute to the mark of the volumetric flask.

11 Test report

The work carried out by the testing laboratory shall be covered by a report that accurately, clearly and unambiguously presents the test results and all other relevant informations. The test report shall be issued separately or in conjunction with the report from the subsequent analytical method. Either of these shall include the following information:

- a) a reference to this European Standard;
- b) complete identification of the sample;

- c) information about the pre-treatment and extraction of the sample;
- d) any detail not specified in this European Standard, or which are optional;
- e) any other information pertinent to the quality of the analytical data.

The test report may include the following information:

- a) information about the sampling and sample pre-treatment;
- b) results of the analytical determinations carried out according to other methods on the same samples, if any.

NOTE: The final report should include all results and relevant information on the sampling, the digestion method and the analytical methods used.

Where the test is not carried out in accordance with this standard, reference may only be made to EN xxxx:2003 in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reasons for the deviations.